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# Prediction of the quaternary eutectic ☆

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**Abstract**

In this work a method is proposed for calculation of the quaternary eutectic using data from binary and ternary systems. The eutectic is determined from the intersection of the four surfaces of primary crystallization of the components. The equations were examined for the system Cd–Pb–Sn–Bi. As the presence of the perutectic compound $Pb_3Bi$ has essentially no influence on the liquidus surface, pure Bi (1), Pb (2), Sn (3) and Cd (4) were used as components of this system. The calculated and experimental values of the fusion temperature and composition of the quaternary eutectic are compared below:

| | $T$/K | $Z_1$ | $Z_2$ | $Z_3$ | $Z_4$ |
|---|---|---|---|---|---|
| Experimental data | 342 | 0.194 | 0.231 | 0.417 | 0.158 |
| Calculated data | 349 | 0.222 | 0.227 | 0.408 | 0.143 |

Good agreement is observed between the calculated and experimental values of the coordinates of the quaternary eutectic.

*Keywords:* Binary eutectic; Multicomponent systems; Phase diagram; Quaternary eutectic; Ternary eutectic

## 1. Introduction

The experimental determination of phase diagrams of multicomponent systems takes quite a long time. A series of equations has been derived for theoretical prediction

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of the ternary eutectic temperature and composition [1]. The equations for direct calculation of the eutectic in pseudoternary systems formed by non-molecular compounds are derived in refs. [2] and [3].

## 2. Method

The possibility of correct calculation of the quaternary eutectic from data of boundary ternary systems is studied in this work. The proposed method consists in determining a quaternary eutectic from the intersection of the four hypersurfaces of primary crystallization of the components or alloys on its base. For a primary crystallization field which is volumetric in the quaternary system, linear addition of the liquidus temperature is used [1].

The quaternary eutectic system has four volumes of primary crystallization which are defined on the linear model from the values of the fusion temperatures of pure components and of the coordinates of binary and ternary eutectics (Fig. 1):

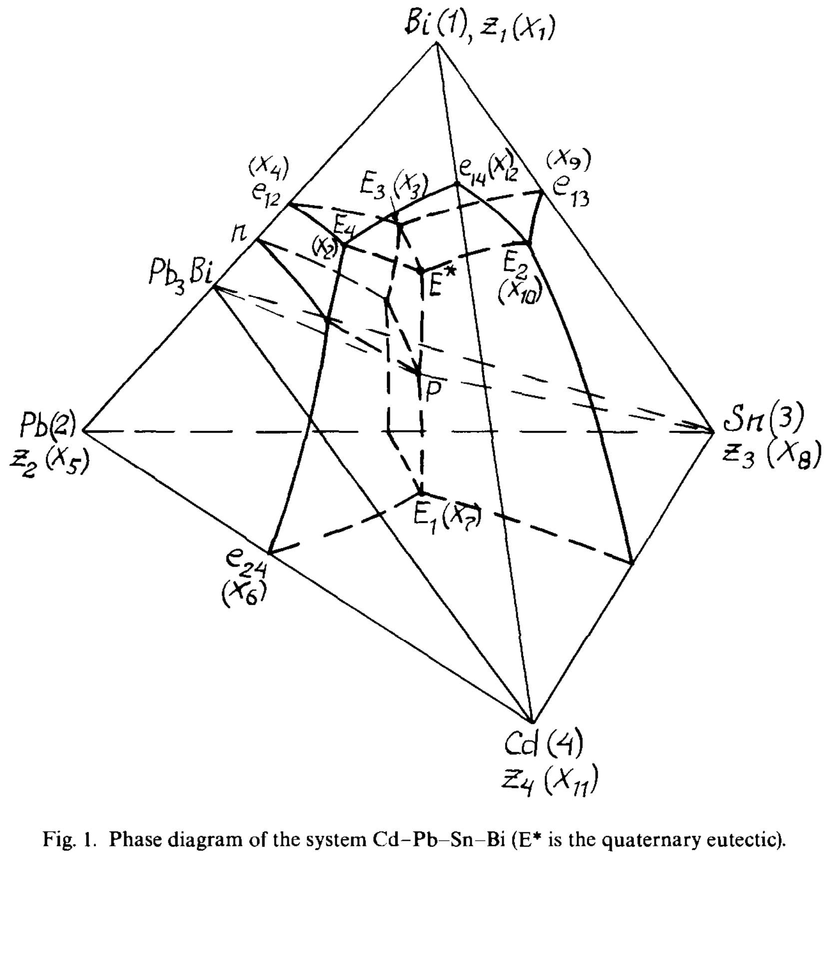


Fig. 1. Phase diagram of the system Cd–Pb–Sn–Bi (E* is the quaternary eutectic).

$$
\begin{aligned}
T &= x_1 T_1 + x_2 T_2 + x_3 T_3 + x_4 T_4 \\
T &= x_5 T_5 + x_6 T_6 + x_2 T_2 + x_7 T_7 \\
T &= x_8 T_8 + x_9 T_9 + x_3 T_3 + x_{10} T_{10} \\
T &= x_{11} T_{11} + x_{12} T_{12} + x_2 T_2 + x_{10} T_{10}
\end{aligned}
\quad (1)
$$

For example, in the first equality $T_1$, $T_2$, $T_3$, $T_4$ and $x_1$, $x_2$, $x_3$, $x_4$ are coordinates of pure component 1, binary and ternary eutectics in the corresponding simple codified subsystem.

The coordinates ($Z$) of system 1–2–3–4 are bound with coordinates ($x$) of its codified subsystem by the matrix $M_j$ in the expression

$$Z = M_j x_i \quad (2)$$

The matrix for the liquidus for component 1 may be written as:

$$M_1 = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{pmatrix} = \begin{pmatrix} 1 & K_1 & K_2 & K_3 \\ 0 & K_4 & K_5 & K_0 \\ 0 & 0 & K_7 & 0 \\ 0 & K_8 & 0 & 0 \end{pmatrix} \quad (3)$$

where $a_{1i}$, $a_{2i}$, $a_{3i}$ and $a_{4i}$ are the mole fractions of components 1, 2, 3 and 4 at points bi-pure component 1, $E_4$–eutectic 1–2–4, $E_3$–eutectic 1–2–3, and $e_{12}$–eutectic 1–2; $K_1$, $K_4$ and $K_8$ are the mole fractions of components 1, 2 and 4 in the ternary eutectic 1–2–4; $K_2$, $K_5$ and $K_7$ are the mole fractions of components 1, 2 and 3 in the ternary eutectic 1–2–3 and $K_3$ and $K_6$ are the mole fractions of the compenents 1 and 2 in binary eutectic 1–2.

The dependence of $x$ on $Z$ is given by:

$$x_i = M_j^{-1} Z \quad (4)$$

where $M_j^{-1}$ is a reverse matrix.

The reverse matrix for the hypersurface of primary crystallization of component 1 may be written as:

$$M_1^{-1} = \begin{pmatrix} 1 & -\frac{K_3}{K_6} & -\frac{(K_2K_6 - K_3K_5)}{K_6K_7} & \frac{K_3K_4 - K_1K_6}{K_6K_8} \\ 0 & 0 & 0 & \frac{1}{K_8} \\ 0 & 0 & \frac{1}{K_7} & 0 \\ 0 & \frac{1}{K_6} & -\frac{K_5}{K_6K_7} & -\frac{K_4}{K_6K_8} \end{pmatrix} \quad (5)$$

By analogy we derived the expressions of the reverse matrix for the hypersurface of primary crystallization of components 2, 3 and 4 using the coordinates of the corresponding binary and ternary eutectics:

$$M_2^{-1} = \begin{pmatrix} -\dfrac{(K_4K_{10}-K_8K_9)}{K_1K_{10}} & 1 & -\dfrac{K_{11}K_{10}-K_9K_{13}}{K_{10}K_{12}} & -\dfrac{K_9}{K_{10}} \\ -\dfrac{K_8}{K_1K_{10}} & 0 & -\dfrac{K_{13}}{K_{10}K_{12}} & \dfrac{1}{K_{10}} \\ \dfrac{1}{K_1} & 0 & 0 & 0 \\ 0 & 0 & \dfrac{1}{K_{12}} & 0 \end{pmatrix} \tag{6}$$

where $K_9$ and $K_{10}$ are mole fractions of components 2 and 4 in the binary eutectic 2–4 and $K_{11}$, $K_{12}$ and $K_{13}$ are the mole fractions of components 2, 3 and 4 in ternary eutectic 2–3–4.

$$M_3^{-1} = \begin{pmatrix} -\dfrac{K_{15}}{K_{14}} & -\dfrac{K_7K_{14}-K_2K_{15}}{K_5K_{14}} & 1 & \dfrac{K_{14}K_{17}-K_{15}K_{16}}{K_{14}K_{18}} \\ \dfrac{1}{K_{14}} & -\dfrac{K_2}{K_5K_{14}} & 0 & -\dfrac{K_{16}}{K_{14}K_{18}} \\ 0 & \dfrac{1}{K_5} & 0 & 0 \\ 0 & 0 & 0 & \dfrac{1}{K_8} \end{pmatrix} \tag{7}$$

Where $K_{14}$ and $K_{15}$ are the mole fractions of components 1 and 3 in binary eutectic 1–3 and $K_{16}$, $K_{17}$ and $K_{18}$ are the mole fractions of components 1, 3 and 4 in ternary eutectic 1–3–4.

$$M_4^{-1} = \begin{pmatrix} -\dfrac{K_{20}}{K_{19}} & -\dfrac{K_1K_{20}-K_8K_{19}}{K_4K_{19}} & -\dfrac{K_8K_{19}-K_{16}K_{20}}{K_{17}K_{19}} & 1 \\ \dfrac{1}{K_{19}} & -\dfrac{K_1}{K_4K_{19}} & -\dfrac{K_{16}}{K_{17}K_{19}} & 0 \\ 0 & \dfrac{1}{K_4} & 0 & 0 \\ 0 & 0 & \dfrac{1}{K_{17}} & 0 \end{pmatrix} \tag{8}$$

Where $K_{19}$ and $K_{20}$ are the mole fractions of components 1 and 4 in binary eutectic 1–4. From the equalities

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix} = M_1^{-1} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix}; \quad \begin{pmatrix} x_5 \\ x_6 \\ x_2 \\ x_7 \end{pmatrix} = M_2^{-1} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix}; \quad \begin{pmatrix} x_8 \\ x_9 \\ x_3 \\ x_{10} \end{pmatrix} = M_3^{-1} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix};$$

$$\begin{pmatrix} x_{11} \\ x_{12} \\ x_2 \\ x_{10} \end{pmatrix} = M_4^{-1} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix}$$

for example it follows that

$$x_1 = Z_1 - \frac{K_3}{K_6} Z_2 - \frac{K_2 K_6 - K_3 K_5}{K_6 K_7} Z_3 + \frac{K_3 K_4 - K_1 K_6}{K_6 K_8} Z_4;$$

$$x_2 = \frac{1}{K_8} Z_4; \quad x_3 = \frac{1}{K_7} Z_3; \quad x_4 = \frac{1}{K_6} Z_2 - \frac{K_5}{K_6 K_7} Z_3 - \frac{K_4}{K_6 K_8} Z_4 \tag{9}$$

By substituting the expressions for $x_i$ into Eq. (1) the following equations are obtained for calculation of the quarternary eutectic:

$$\begin{cases} A_1 Z_1 + A_2 Z_2 + A_3 Z_3 + A_4 Z_4 = T \\ A_5 Z_1 + A_6 Z_2 + A_7 Z_3 + A_8 Z_4 = T \\ A_9 Z_1 + A_{10} Z_2 + A_{11} Z_3 + A_{12} Z_4 = T \\ A_{13} Z_1 + A_{14} Z_2 + A_{15} Z_3 + A_{16} Z_4 = T \\ Z_1 + Z_2 + Z_3 + Z_4 = 1 \end{cases} \tag{10}$$

Where $T$, $Z_1$, $Z_2$, $Z_3$ and $Z_4$ are the temperature and the mole fractions of components 1, 2, 3 and 4 in the quaternary eutectic,

$$A_1 = T_1, \quad A_2 = \frac{T_4 - T_1 K_3}{K_6}, \quad A_3 = \frac{T_3 K_6 - T_4 K_5 - (K_2 K_6 - K_3 K_5) T_1}{K_6 K_7},$$

$$A_4 = \frac{T_2 K_6 - T_4 K_4 + (K_3 K_4 - K_1 K_6) T_1}{K_6 K_8},$$

$$A_5 = \frac{T_2 K_{10} - T_6 K_8 + (K_8 K_9 - K_4 K_{10}) T_5}{K_1 K_{10}}$$

$$A_6 = T_2, \quad A_7 = \frac{T_7 K_{10} - T_6 K_{13} + (K_9 K_{13} - K_{10} K_{11}) T_5}{K_{10} K_{12}}, \quad A_8 = \frac{T_6 - T_5 K_9}{K_{10}}$$

$$A_9 = \frac{T_9 - T_8 K_{15}}{K_{14}}, \quad A_{10} = \frac{T_3 K_{14} - T_9 K_2 + T_8 (K_2 K_{15} - K_7 K_{14})}{K_5 K_{14}}$$

$$A_{11} = T_3, \quad A_{12} = \frac{T_{10} K_{14} - T_9 K_{16} + (K_{15} K_{16} - K_{14} K_{17}) T_8}{K_{14} K_{18}}$$

$$A_{13} = \frac{T_{12} - T_{11} K_{20}}{K_{19}}, \quad A_{14} = \frac{T_2 K_{19} - T_{12} K_1 + (K_8 K_{19} - K_1 K_{20}) T_{11}}{K_4 K_{19}}$$

$$A_{15} = \frac{T_{10} K_{19} - T_{12} K_{16} + (K_{16} K_{20} - K_8 K_{19}) T_{11}}{K_{17} K_{19}}, \quad A_{16} = T_{10}$$

## 3. Results

Eqs. (10) were examined for the system Cd–Pb–Sn–Bi [4, 5]. Because the presence of the perutectic compound $Pb_3Bi$ has essentially no influence on the liquidus surface (Fig. 1), Bi (1), Pb (2), Sn (3) and Cd (4) were used as components of the system. The calculated and experimental values of the fusion temperature and composition of the quaternary eutectic are compared below:

| | $T$/K | $Z_1$ | $Z_2$ | $Z_3$ | $Z_4$ |
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| Experimental data [4, 5] | 342 | 0.194 | 0.231 | 0.417 | 0.158 |
| Data calculated using Eqs. (10) | 349 | 0.222 | 0.227 | 0.408 | 0.143 |

There is good agreement between the calculated and experimental values of the coordinates of the quaternary eutectic.

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